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EVALUATION OF PROPERTIES OF BORON-ZIRCONIUM GLAZES USING STATISTICAL METHODS

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The authors propose a generalization of compositions and a mathematical estimate of the effect of individual components on properties of opacified boron-zirconium glazes. The equations obtained make it possible to calculate the TCLE, whiteness, luster, and microhardness of glazes based on their compositions, compare properties of known and newly developed glazes, and make assumptions on the mechanism of phase formation processes, which determine the properties of glaze coatings. The mathematical models are based on the effect exercised on glaze properties not by single oxides, but by binary and ternary compounds arising in boron-zirconium coatings.

The expanding available information on the technology of glaze coating for ceramics makes collecting data on glaze compositions and properties increasingly labor-consuming, since glazes are usually developed for specific production conditions with the aim of improving a particular property of the coating. As a consequence, the known glaze compositions are currently numbered in the hundreds, and their multicomponent compositions significantly complicate a comparative analysis of their properties and process parameters. Boron-zirconium glazes make up substantial share of known glazes, and their abundance is due to the wide application of fast firing technologies in ceramic tile production and the variety of ceramic mixture compositions used in tile production. At the same time, there is still no comprehensive theoretical model for the composition of glaze coatings or quantitatively justified criteria for using particular oxides in developing new compositions, and mathematical dependences correlating certain properties of coatings to the effect of a single oxide or a group of oxides in the coating composition have still not been discovered.

We made an attempt to generalize the compositions and give a mathematical evaluation of the effect of single components on the properties of opacified boron-zirconium glazes with the aim of finding the range of their optimum values. In this case, the most promising approach could be using mathematical statistical methods in data processing, which will make it possible if not to disclose the mechanism of the influence of a particular component on the particular property, then at least to reveal the degree of its effect and more accurately determine the direction of the search [1]. The following main properties of glaze coatings were selected as the correlation parameters: TCLE, microhardness, whiteness, and luster.

The field of the considered glaze compositions was developed on the basis of patents (authors' certificates) and other published data, and as a result, not every glaze composition was characterized by a complete set of properties. The glaze compositions included oxides of 19 elements (hereafter these oxides in our formulas are designated by chemical elements) and fluorine in such compounds as CaF_2, AlF_3, Na_2SiF_6, and Na_3AlF_6 . In order to obtain reliable mathematical dependences, the effect on the TCLE and luster was assessed not taking into account the compositions containing Li_2O, SO_3, P_2O_5, and CuO. The effect of oxides on whiteness was assessed for compositions not containing MnO. In assessing microhardness, the compositions containing MnO and PbO were excluded as well, being the components of the extreme effect. The molar content of oxide was measured in percent, which later on made it possible to infer some conclusions on structural ratios of the components.

After a preliminary selection, a data file of 214 compositions was formed. The largest number of points suitable for analysis in this data file corresponds to the TCLE (174 points); there are 99 points for evaluation of whiteness, and 86 points for luster evaluation. The smallest number of points was found for the assessment of the effect of components on microhardness. Compositions having less than 3 nonzero parameters were excluded from the analysis, and their effect was considered only after obtaining a reliable mathematical dependence from other components, which increased the total reliability of the model. The distribution of the points with nonzero values for individual components in the glaze compositions is shown in Fig. 1. Using the obtained

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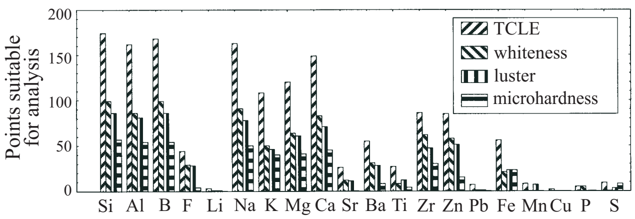

Fig. 1. Distribution of the number of points suitable for analysis based on glaze components.

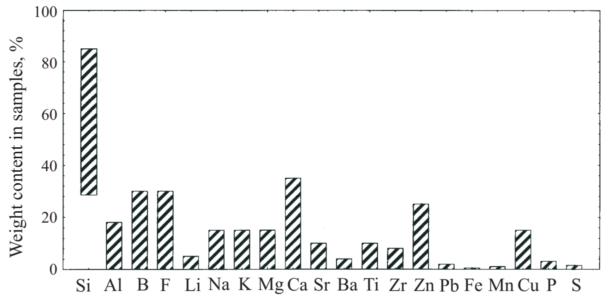

Fig. 2. Variation bounds of component content in glazes.

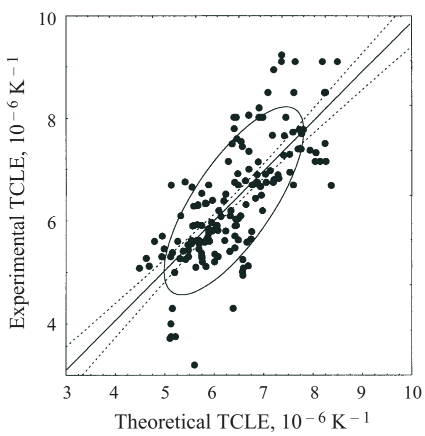

Fig. 3. Characteristics of the model for TCLE of glaze.

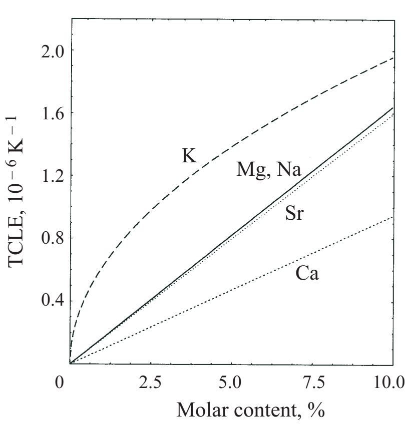

Fig. 4. The effect of alkaline and alkaline-earth oxides on variation in TCLE.

dependences, one should bear in mind that they are derived within certain limits of the component weight content (Fig. 2).

It was established for all four indicators of properties that each indicator is an independent value and is not related by a dependence to the other parameters. Due to the preset measurement limits (0 – 100%), the indicators of whiteness and luster of coatings required the introduction of additional transition values in order to eliminate nonlinear distortions in the ranges close to the boundary values (0 and 100%):

$$IW = \ln\left(\frac{\text{Whiteness}}{100 - \text{Whiteness}}\right);$$

$$IL = \ln\left(\frac{\text{Luster}}{100 - \text{Luster}}\right),$$

where *IW* and *IL* are the respective indicators of whiteness and luster.

Based on the statistical processing of data files, a mathematical model of the effect of the components on glaze-coating properties was obtained for each indicator. The ellipses in Figs. 3 – 5 indicate the 80% confidence interval of point distribution, the theoretical straight line, and the 95% interval of its variation. In order to avoid large errors in calculations, it is desirable not to exceed the parameter values by more than 30% of the limits indicated in Figs. 3 – 5.

Considering each expression in the mathematical context, certain conclusions can be inferred with respect to structural groups of oxides in the melt and, accordingly, technological recommendations can be given for determining the optimal components for glaze compositions. It should be noted that the obtained dependences suggest a new concept of the effect of certain components on coating properties.

TCLE. The mathematical model of the effect of components on the TCLE of glaze is represented in the form of an equation, in which the determination coefficient is 0.573, which is quite reliable for the considered data file (Fig. 3):

$$\begin{gathered}\text{TCLE} = 5.54 - 1.49(1 - 0.116\text{Na})(1 - 0.116\text{Mg}) + \\ 0.621\sqrt{\text{K}} + 0.0948\text{Ca} + 0.16\text{Sr} - 0.0177(\text{B} + 2\text{Al}) + \\ 0.0283(2\text{Zr} - \text{Zn}) + 1.893[\text{Fe} - 3.54\text{Mn}(1 + 0.0922\text{Ti})].\end{gathered}$$

In constructing this model, the effect of silicon, barium, and lead oxides, as well as fluorine, was found to be statistically insignificant. At the same time, it was found necessary to study separately the role of alkaline and alkaline-earth metal oxides. Analyzing the particular dependence of the TCLE on the content of R_2O and RO, which agrees with the known propositions [2], we observe their essentially positive, but different effect on this property, which calls for distinguishing them as a separate group. In particular, it was found that the potassium oxide effect in this group is the most significant, whereas the calcium oxide effect is the least significant, and both dependences are nonlinear. The degree

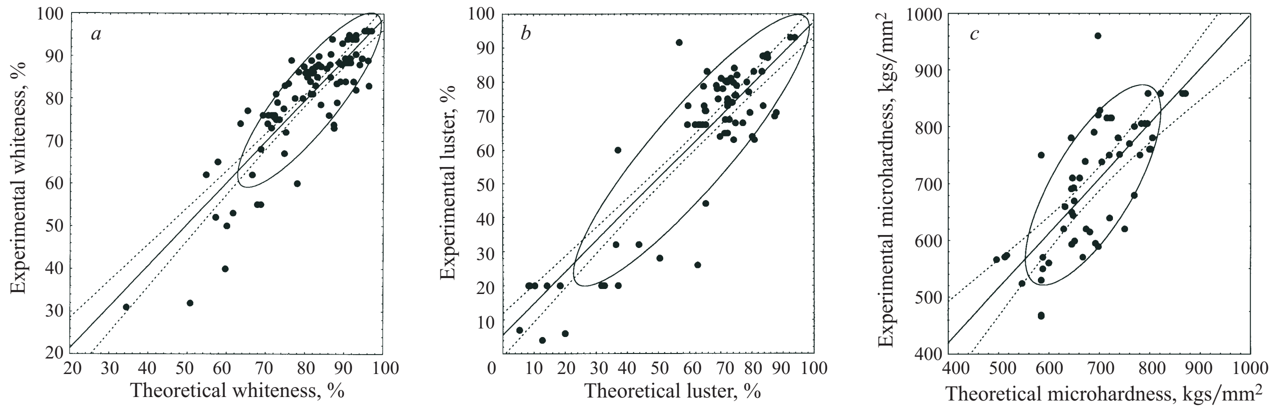

Fig. 5. Characteristics of models for whiteness (*a*), luster (*b*), and microhardness (*c*) of glaze.

of the effect of sodium, magnesium, and strontium oxides is approximately equal and nearly linear (Fig. 4).

Furthermore, it follows from the above formula that the effect of magnesium and sodium oxides is interdependent, and when the molar content of one of the components is 8.6%, the effect of the other component on the TCLE is totally absent. Such a dependence suggests that in the presence of liquation, a reaction with the formation of binary alumosilicate or sodium-magnesium diborate can take place in the melt, which affects to a great extent the TCLE of the whole composition.

Based on the specified formula, it can be inferred that the aluminum oxide effect is two times stronger than that of boron oxide. This is presumably related to the formation of the compound $B_2O_3 \cdot 2Al_2O_3$, which is responsible for the modification of the TCLE. An additional analysis showed also that the formation of compounds of the type of $ZnO \cdot B_2O_3$ or $ZnO \cdot Al_2O_3$ is possible, since the elimination of the term depending on boron oxide and aluminum oxide yields a decrease of the Student coefficient related precisely to the term in the equation containing zinc and zirconium oxides.

The effect of zinc and zirconium oxides can be attributed to a separate group, since it is antibatic: an increase in the amount of one of these elements compensates for the effect of the other element. With the ratio of $ZnO : ZrO_2$ equal to 2 : 1, the leading effect of zinc on the TCLE of the composition is observed.

The calculations show that in spite of the known partial factors [3], the effect of iron, manganese, and titanium oxides is nearly 10 times higher than that of alkaline and alkaline-earth oxides, whereas titanium dioxide present in the complex of the specified oxides intensifies the effect of manganese oxide but does not exercise an independent effect on the TCLE. It is also probable that copper oxide has a negative effect on the TCLE, whose value is comparable to the effect of alkaline oxides.

Whiteness. It should primarily be noted that such oxides as CaO and MgO, which are known in technology as components facilitating an increase in glaze whiteness, in the considered field of compositions do not have a statistical effect on this indicator:

$$IW = 1.76 - 0.0515(\mathrm{Ba} \cdot \mathrm{Na}) + 0.00229(\mathrm{Si} \cdot \mathrm{Na}) - 0.895\mathrm{Pb} - 0.544(1 - 0.213\mathrm{Zn})(1 - 0.213\mathrm{Zr}) + 0.022\{\mathrm{F} - 2\mathrm{B} + 4.9\mathrm{Al}[1 + 0.095(\mathrm{K} - \mathrm{Na})]\}.$$

At the same time, the above equation (determination coefficient is 0.712, Fig. 5*a*) indicates that the whiteness of a glaze can be improved by the simultaneous presence of a complex of boron, aluminum, potassium, and sodium oxides and fluorides, although complicated interrelationships exist within this complex. In our opinion, these mutual influences can be related to the process of liquation arising within the considered limits of the content of particular components. The positive effect of silicon dioxide together with sodium oxide on whiteness is insignificant; however, it can be calculated. Taking into account the possibility of increasing the determination coefficient by 2%, it was established that titanium dioxide has an additional effect on the coating whiteness.

The effect of zinc oxide and zirconium dioxide on increasing whiteness is mutually complementing, i.e., considering that only pairwise correlation is present in the equation, it can be assumed that the joint effect of these oxides to a great extent exceeds the effect exercised by each individual component. An increase in the molar content of zinc oxide or zirconium dioxide decreases the degree of effect of any of these components, and when one of them is present in the amount of 4.7%, the other component has no effect on whiteness. It is interesting that this fact established in the calculations fully agrees with the composition of glaze with a decreased zirconium dioxide content, which was developed by us earlier (USSR Inventor's Certif. No. 1609754).

Lead oxide has the strongest negative effect on glaze whiteness. An increase in its molar content up to 10% decreases the whiteness indicator by 30 – 40%. Barium oxide has a negative effect as well, but to a lesser degree and only in the presence of sodium oxide.

Luster. The glaze luster indicator is a complicated parameter of coatings, which is hard to estimate. The determination coefficient for the regression equation describing the

TABLE 1

Component	Determination coefficient	Confidence interval	t-Criterion
Statistical parameters of components not included in the luster model			
K	– 0.089	0.035	2.52
Ba	0.145	0.066	2.2
Ti	0.0736	0.028	2.61
Pb	0.404	0.228	1.76
S	22.8	7.4	3.11
Li	0.199	0.13	1.52
F	0.0165	0.0082	2.02
Statistical parameters of components not included in the microhardness model			
Na	– 10.99	3.4	3.2
Sr	48.9	16.7	2.7
Ba	25.9	10.6	2.4
B	2.82	1.28	2.2
F	3.61	1.6	2.24

luster indicator is 0.769, which is evidence of the high reliability of the developed model (Fig. 5*b*):

$$IL = 1.212 - 0.124(Mg + Ca) + 0.0999Al + [0.0196(Mg + Ca) - 0.0668Zn]Zr + 0.00877(Zn \cdot B).$$

It can be seen that the complex of calcium and magnesium oxides has the most significant negative effect on luster, possibly due to their active mineralizing effect on the glaze melt, which leads to surface crystallization and the formation of a dull surface.

The presence of aluminum oxide and the joint presence of zinc and boron oxides have an obvious positive effect. Zinc oxide, by weakening the effect of alkaline-earth oxides in the presence of zirconium dioxide, has a positive effect on the luster parameter.

It should be noted that the degree of influence of other glaze components on luster is below the significance level; however, this is not sufficient for totally excluding them from consideration (Table 1). With a greater amount of available data, it could be possible to clarify the role of sodium, strontium, and iron oxide and the joint effect of fluorine and boron oxide.

Microhardness. Despite the significantly smaller number of data on microhardness (only 54 points), their processing made it possible to obtain a sufficiently reliable mathematical dependence of this property on the glaze composition. The determination coefficient for the regression equation describing microhardness amounted to 0.60 (Fig. 5*c*):

$$M = 581 + 48.6(Fe \cdot Al) + 0.0771Si(Mg + Ca) + 4.17Zr(Al - 2.5K) + 6.68Zn.$$

The interpretation of the role of oxides participating in the regression equation well agrees with the formation of structural complexes of the spinel type $Fe_2O_3 \cdot Al_2O_3$, diopside $CaO \cdot MgO \cdot 2SiO_2$, and baddeleyite ZrO_2 in the glaze coating, whose effect on increasing microhardness is beyond question. It is worth noting that zinc oxide has an independent positive effect on microhardness. These facts were also corroborated by the compositions developed by us for zirconium-free glazes with high microhardness parameters (Ukraine Patent No. 22415A).

The most evident negative effect is exercised by potassium oxide, which weakens the effect of aluminum oxide and zirconium dioxide. An additional effect of individual components was established for certain components after refined calculations (Table 1).

All the above modifies the traditional ideas of necessarily using various components in short supply in production of boron-zirconium glazes in order to accomplish high parameters in their properties. At the same time, it is noteworthy that zinc oxide plays a significant role in all four regression equations, and its molar content within the limits of 5 – 10% contributes to the production of glazes with high service parameters. The mathematical models of glaze properties give priority not to the effect of single oxides but to the effect of binary and ternary compounds formed in boron-zirconium coatings and explain, in particular, the significant inaccuracies in the estimated TCLE values calculated using the partial factor method. The obtained mathematical dependences make it possible to estimate with higher precision the value of this property for new glaze compositions.

These data call for a new approach to the research and development of the compositions of multicomponent boron-zirconium glazes. Thus, based on the obtained dependences, it is possible to make assumptions on the phase-formation processes, which determine the properties of glaze coatings. The specified dependences make it possible to estimate the main properties of glazes when their compositions are known, and on this basis to make a sufficiently reliable comparison of the properties of known and newly developed glazes, without performing a great number of experiments.

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